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14. ABSTRACT
With the growing demand in the reduction of size of semiconductor devices, understanding the chemistry and physics at the atomistic level is becoming an essential part in the design of devices based on electronic materials. One of the major challenges in this area is to obtain desired surface morphology of a thin-film by controlling external parameters, such as temperature pressure etc. The smoothness of a thin-film surface depends on rate of surface diffusion of the adatoms during a growth process. Enhancing surface diffusion can lead to a smooth film. In other words, the rate of surface diffusion will depend on how strongly the adatoms bound to surface. Reducing binding energy of the adatoms with the surface will result enhanced surface diffusion. In the present work, we have shown how application of an external field can be used to control binding energy. First-principle calculations have been performed to calculate the binding energies at different field strength and orientation, followed by Kinetic Lattice Monte Carlo simulations to obtain surface microstructure. Using the above methods we have established a correlation between the external field (strength and orientation) and microstructure of GaN thin-film in MBE process. We have shown that by controlling the strength and orientation of the external field, one can obtain GaN thin-film with desired roughness.

15. SUBJECT TERMS
Expitaxy, Gallium Nitride, ab initio, KLMC, surface diffusion, external field, bond energy

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1. INTRODUCTION

With the growing demand in the reduction of size of semiconductor devices, understanding the chemistry and physics at the atomistic level is becoming an essential part in the design of devices based on electronic materials. One of the current challenges within the semiconductor industry is to fabricate semiconductor materials with desired properties. It is well known that the properties of the thin-films grown by epitaxy are highly dependent on the macroscopic growth conditions, such as temperature, pressure, and precursor composition. These macroscopic parameters also have profound effect on the phenomenon at the atomic level. A change in the microstructure of the thin-film is intimately related to the change in the properties of the materials. For example, the non-ideal growth condition can result in defects, such as non-crystalline atomic arrangements and antisite defects. While it is generally accepted that the macroscopic conditions of growth affect the microstructure of the film, current understanding of the precise relationship between reactor-scale variables and the microstructure is limited. Increase in our knowledge of the this relationship will allow development of methods and means to control the microstructure of films, which is key to developing materials with desired electronic properties.

In currently used growth techniques, the precursor molecules (or atoms) are injected into the reactor. These precursors then react in the gas phase and at the surface of the wafer to deposit thin-film of the material. The growth rate, uniformity, electrical and mechanical properties are dependent on the kind of precursors used, gas and wafer temperature, and the reactor pressure. A change in the temperature and pressure results in a change in the rate of chemical reaction and the diffusion of the atoms and molecules on the surface that ultimately lead to different microstructures of the thin-film. Since the rate of a reaction is dependent on the activation barrier of the reaction, the effect of temperature manifests itself as a change of activation barriers of the reaction. This implies that the microstructure of the film can be controlled if one can control the activation barriers of chemical reaction by some means. Recent studies [1] have shown that the application of an external electric field often results in microstructures, which are better than their counterpart, which were grown without any external field. While the results of such studies are extremely promising, they are very limited. More importantly, it is not well understood. The purpose of the study is to determine the relation between the applied external field and microstructure of the material.

One of the most conceptually simple techniques for growing thin-films is molecular beam epitaxy (MBE). In this technique, atomic species that the material is composed of are injected directly. The adatoms are adsorbed directly on the surface. Growth occurs when the atoms move to a step site where the total bond energy is much greater than the bond energy of the flat surface. At relatively low temperatures, the adatoms do not have enough energy to overcome the activation barrier for diffusion. Consequently they are unable to move on the surface to reach the appropriate sites for growth. Since the activation barrier for diffusion is proportional to the bond energies of the adatom with the initial and final surface site, the surface mobility is controlled by the residual bond energy. There are several reports in the literature, which suggest the surface diffusion of the adatoms is crucial to the film-growth [1-5]. The essential idea behind the work is, therefore, to control the bond energy by application of external field.

In the present work, we calculate the bond energies of the adatom at different sites on the surface in the presence of an external field using first principle atomistic modeling such as ab initio quantum chemistry. We will then perform Kinetic Lattice Monte Carlo (KLMC) simulation to obtain microstructural details. The ab initio calculations for bond energies are performed for various orientation and strength of the field, and the calculated bond energies are used as inputs for KLMC calculations. We expect that a parametric study of bond energy as a function of the strength and orientation of the external field, followed by KLMC calculations will provide the necessary relationship between the quality of grown film and applied external field. Gallium Nitride (GaN), a promising wide-bandgap semiconductor material, will be studied as an example. Although, MOVPE is the most commonly used commercial technique for depositing thin-films of III-V materials, we have restricted our Phase I study to a MBE on account of the time constraints of the project.

2. PHASE I TECHNICAL OBJECTIVES

The specific objectives of the Phase I studies are:

- Identify the adsorption site of the GaN surface (such as kink and ledge sites).
- Construct the cluster models of these sites. The cluster model will mimic the actual environment of the actual sites. Cluster models contain smaller number of atoms than the real system, and are necessary to perform ab initio calculation within a realistic period of time. The cluster models will be optimized *via* ab initio method.
- Calculate the bond energies of the adatom with various surface sites with and without external field using ab initio method.
- Calculate the activation barriers for various diffusion processes with and without external field using an ab initio method.
- Perform parametric studies as a function of external field in order to study its effect on activation barriers and bond energies.
- Modify and enhance the existing KLMC computer code in order to study the microstructure of the GaN. This part of the work will be performed in close collaboration with the University of Michigan.
- Perform microstructure analysis with KLMC by supplying as inputs the values of activation barriers and bond energies obtained *via* ab initio method, both in the presence and absence of an external field. This will provide the effect of the external field on the quality of the grown film by MBE.
- Time permitting, perform, preliminary bond energy calculations related to MOVPE of GaN in order to create the foundation for Phase II work.

3. PHASE I WORK

In epitaxial growth process, when atoms arrive at the substrate, they can adsorb, incorporate into the crystal, migrate on the surface, interact with other atoms or desorb (Figure 1). The primary controllable factors that affect this process are the surface structure, the temperature of the substrate, and the incident fluxes. In order to grow high quality film, the atoms on the flat surface must be able to move and reach sites where growth can take place. A smooth film is desired for microelectronics applications. In order to do so, the atoms adsorbed on the flat surface should be able to diffuse to the growth sites (such as kink and ledge sites) where the residual bond energy is much higher. The rate of surface diffusion is dictated by the activation barrier of the process. When the activation barrier is high, the atoms tend to form islands. Since the activation energy of the surface diffusion process is related to the bond energy of the adsorbed atoms on the surface, and bond energy can be altered by application of external field, one can control activation energies by applying external field. Therefore, in principle, it is possible to obtain desired surface morphology of the film by varying the strength and orientation of the field. **The goal of the project is to predict surface morphology of the film with application of an external field. The project aims to control the bond energy by controlling the strength and orientation of the external field. The objective is to determine optimum field strength and its orientation in order to obtain uniform microstructure.**
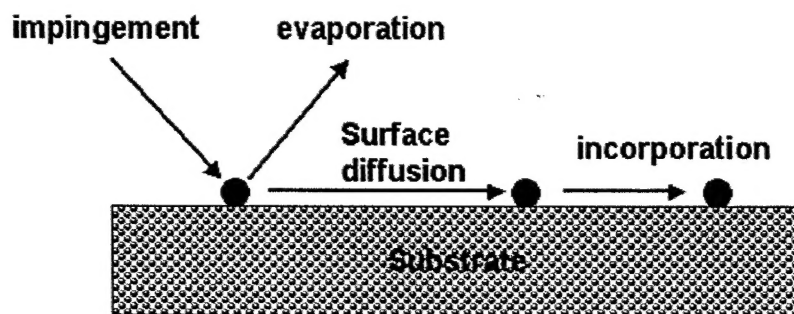
Figure 1. Various surface processes during a MBE growth.

The Phase I project is divided into two parts: 1) calculate the bond energy and the activation barriers in presence of an external field using ab initio quantum chemistry method and 2) perform Kinetic Lattice Monte Carlo (KLMC) calculation by using the calculated bond energies and activation barriers in order to obtain surface morphology. In the following, we present the results that are obtained during the Phase I studies.

4. RESULTS

In the following, we first describe the ab initio quantum chemistry method for calculation of bond energies and activation barrier.

4.1 Ab Initio Quantum Chemistry Calculations:

The ab initio quantum chemistry methods are based on the principle of quantum mechanics, and solution of the Schrodinger equation is performed numerically for a many-electron system. Quantum chemistry methods are widely used for calculation of energy of many electron molecular systems, optimization of molecular geometries, calculations of activation barriers, transition states for chemical reactions, infrared frequencies (or vibrational frequencies), molecular properties (such as dipole moment, polarizability etc.) and thermodynamic properties (such as free energy of a reaction, heat of formation, entropy and enthalpy). [6]

According to quantum mechanics the energy of a system can be evaluated solving the Schrodinger equation [6,7]:

$$H\Psi = E\Psi \tag{1}$$

where Ψ is the wave function of the molecule or atom, H is the Hamiltonian operator and E is the energy of the system. The operator contains the kinetic energy of electrons, electron-electron repulsion, electron-nuclear attraction. *The operator H contains the interaction of the electron cloud in the molecule with the external field, and the energy of the molecule or atom (E) will automatically be evaluated, including the effect of an external field.* Since the above equation cannot be solved exactly for many-electron systems, the quantum chemistry method follows an approximate method to calculate the energy. In the quantum chemistry method, the exact Schrodinger equation is transformed into a determinant equation (Hartree-Fock equation) assuming that the wave-function Ψ is a determinant (known as Slater determinant), which maintains the properties of electron. The elements of the determinant are the molecular orbitals of the molecule. The Hartree-Fock equation is given by [6,7]:

$$\mathbf{F}\varphi_i = \varepsilon_i\varphi_i \tag{2}$$

where $\mathbf{F}$ is the Fock operator and ε_i is the energy of the ith molecular orbital, ϕ_i. The total energy E is then expressed in terms of ε_i as:

$$E = \sum_i \varepsilon_i + exchange\ energy + coulomb\ energy + nuclear - nuclear\ repulsion\ energy \tag{3}$$

In the presence of an external field, the molecular orbitals will be perturbed and the corresponding energy will be different for that without external field. In the present study, we will calculate the energy that includes the effect of a static electric field.
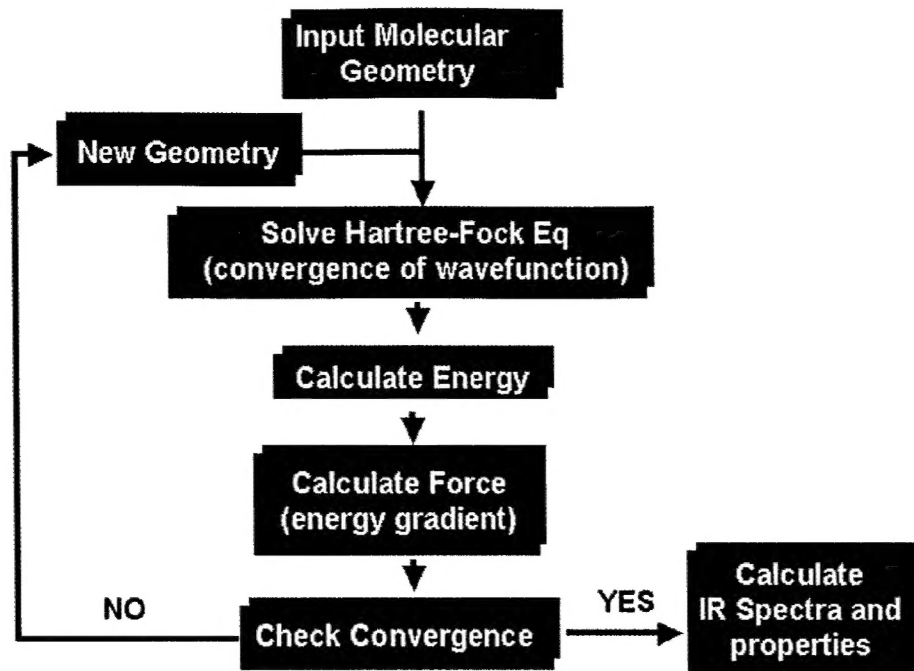
Figure 2. Flow chart for quantum chemistry calculation with GAUSSIAN 98 and GAMESS.

The entire calculation is performed using the commercial code GAUSSIAN 98, [8] Figure 2 shows a flow chart for the calculation procedure.

Bond energy of the bond A---B of a molecule AB (where A and B can be monoatomic and/or polyatomic) is defined as follows:

$$BE = E(A) + E(B) - E(AB) \qquad (4)$$

Where $E(A)$, $E(B)$ and $E(AB)$ are the energies of A, B and AB, respectively. The energies can be calculated using the expression in the equation (4) and following the flow chart in Figure 2. In the following sections, we present the results of our ab initio calculations of bond energies and activation barriers in presence of external field.

4.1.1 Bond Energy Calculations (Single GaN Molecule)

In order to check the proof of the concept, we performed a simple calculation with a single GaN molecule. This molecule exists as $Ga^{+\delta}N^{-\delta}$. This means N is slightly negatively charged due to its stronger ability to pull the bonding electrons (higher *electronegativity*). Consequently Ga becomes positively charged to maintain electroneutrality. Due to their polarity, the polar molecules have a net dipole moment. With application of an external field, the dipole of the molecule will interact with the external field, and reorient itself to minimize the potential energy. Reorientation is possible when the molecules are in the gas phase. In the solid state, since no movement of the molecules is possible, the presence of an external field will either increase or decrease the potential energy of the molecule depending on its orientation.
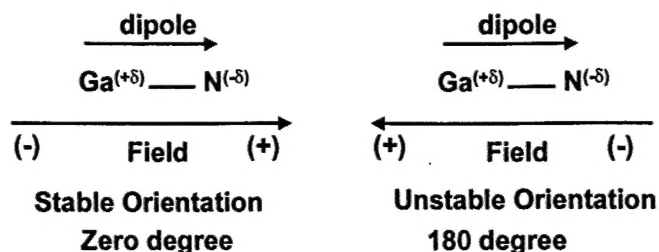
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Figure 3. Definition of the direction of the external field and the molecular dipole moment.
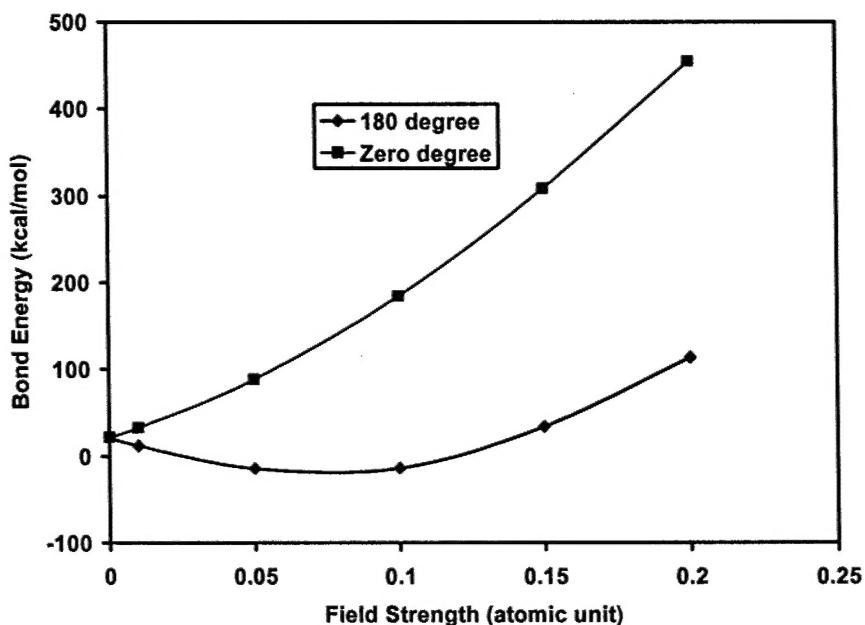

Figure 4. Bond energy of a GaN molecule in the presence of an external field in two difference orientations. This figure displays the proof of the concept that was proposed.

In the present calculation, the positive dipole moment direction of the molecule is defined as pointing from positive to negative while the positive external field is defined as pointing from negative to positive (See Figure 3). When the angle between the two vectors is zero, the negative and positive sides of the field interact with the positively charged Ga atom and negatively charged N atom, respectively (Figure 3). This is a stabilizing interaction, and the potential energy decreases. This means more energy is needed to break this bond. Figure 4 shows that bond energy increases in this orientation. On the other hand, when these two vectors are aligned at zero degree, the interaction is unfavorable, and the potential energy increases when the molecule is not allowed to move. This means the energy needed to break the bond decreases, and our results show that bond energy decreases with an increase in field strength (Figure 4). It is interesting and important that the bond energy passes through a minimum after a critical value of field strength when the field is aligned 180 degree with respect to the dipole moment of the molecule. The following may be the reason for such behavior. In this configuration, positive charge on Ga decreases (and negative on N also decreases). Therefore the electrostatic attraction between Ga and N decreases, and the bond strength decreases. After the critical value of the

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field strength, Ga tends to become more and more negative (and N becomes more and more positive). This again increases the bond strength due to increased electrostatic attraction between the atoms. However, in the other orientation, positive charge on Ga (and negative charge on N) always increases which leads to monotonous increase in the electrostatic attraction. It should be pointed out that bond energy reaches a negative value at the minimum of the curve for a "180 degree" orientation. This means that the molecule will break apart at that particular field strength.

At this stage, with these calculations and the concept, we are in a position to predict the orientation of the field that would decrease the bond energy of a diatomic molecule. We have seen similar trends in HCl (hydrochloric acid) molecule, which is polar like GaN. However, in a polyatomic molecule, situation will be much more complicated due the interaction of various bonds oriented in different directions with respect to the external field.

4.1.2 Bond Energy Calculation and Geometry Optimization (GaN Crystal Using Cluster Model)

In our next task, we have constructed a cluster model of the GaN (100) surface. GaN surface is an infinite solid, and we have chosen a small part of the solid, which mimics the actual (100) plane, in order to save CPU time for quantum chemistry calculations.
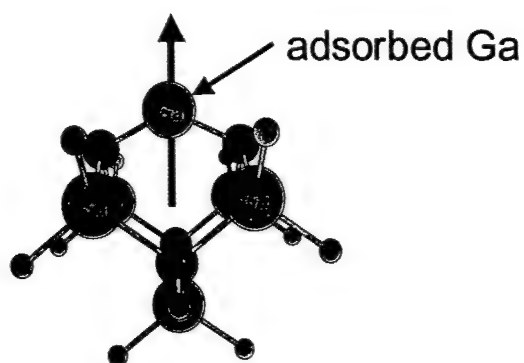
Figure 5. Cluster model for calculation of binding energy of surface Ga.

In the bulk of the crystal every Ga and N atoms are tetrahedrally coordinated to four N and Ga atoms, respectively. In our cluster model, the bulk Ga and N atoms are being saturated by hydrogen atoms in order to save CPU. Figure 5 shows the cluster model used for calculation of bond energy of the adsorbed Ga atom. All other atoms, except the surface Ga atom, were held fixed during the molecular geometry optimization procedure. Figure 6 shows the bond energy variation with the strength and the orientation of the external field. A nearly similar behavior to earlier calculations shown in Figure 4 is obtained in the cluster calculation. When the field points away from the surface, the bond energy decreases up to certain strength of the field. Beyond that it increases sharply. The bond energy is decreased by almost 23% from its no field value. If components of the field vector are taken on the two GaN bonds that the adsorbed Ga makes with the surface (Figure 5), we end up in a situation, which is similar to "180 degree" orientation in Figure 3. This orientation is expected to decrease the bond energy up to certain field strength. On the other hand, when the field points towards the surface, the situation is

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similar to "zero degree" orientation in Figure 3. However, we see a slow increase in the bond energy in case of cluster model when field is pointed towards the surface. This could be an effect of the polyatomic molecular structure.
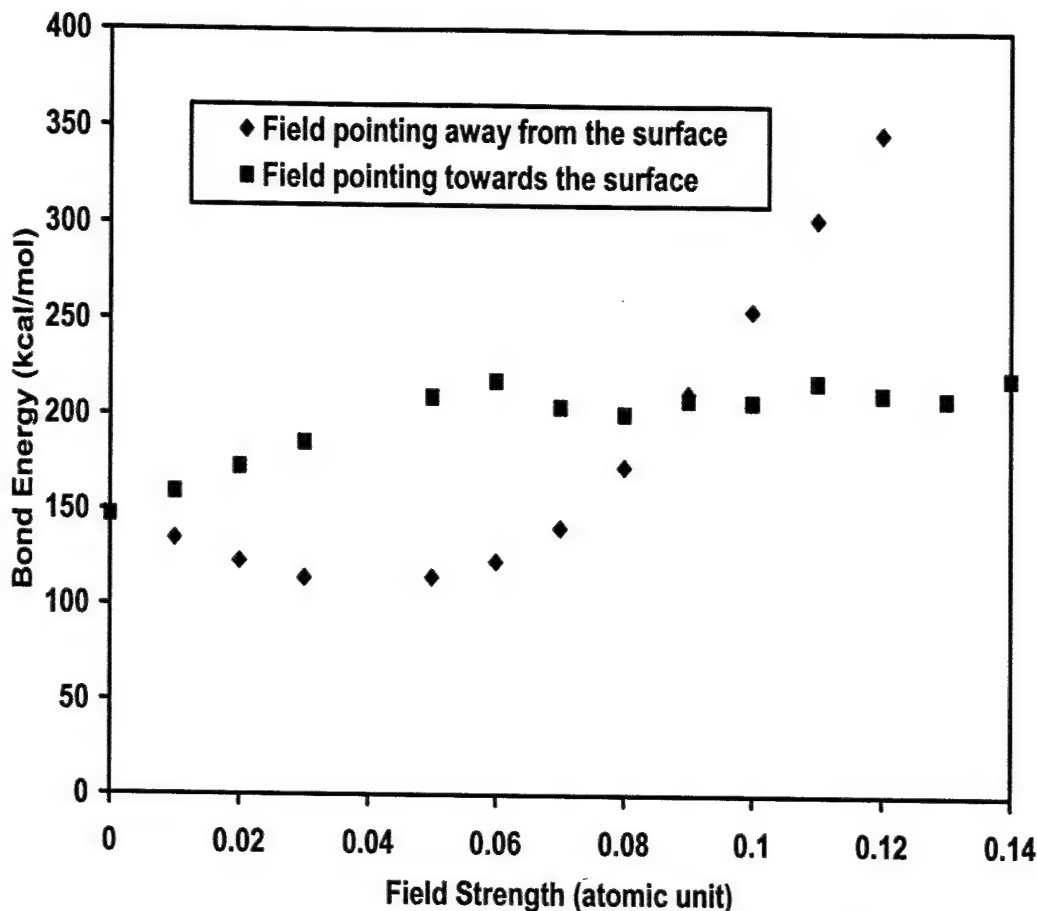

Figure 6. Bond energy of surface Ga in presence of external field in two difference orientations.

4.1.3 Activation Barrier Calculation and Geometry Optimization (Cluster Model):

Activation barrier for diffusion of Ga atoms on the GaN surface has been calculated using ab initio method. Calculations were performed as a function of external field at two different orientations. The cluster model for activation barrier calculations are shown in Figure 7 a. During the geometry optimization, the two GaN bond involving the adsorbed Ga atom are optimized while the rest of the molecule is kept frozen to its crystal structure in order to save CPU.
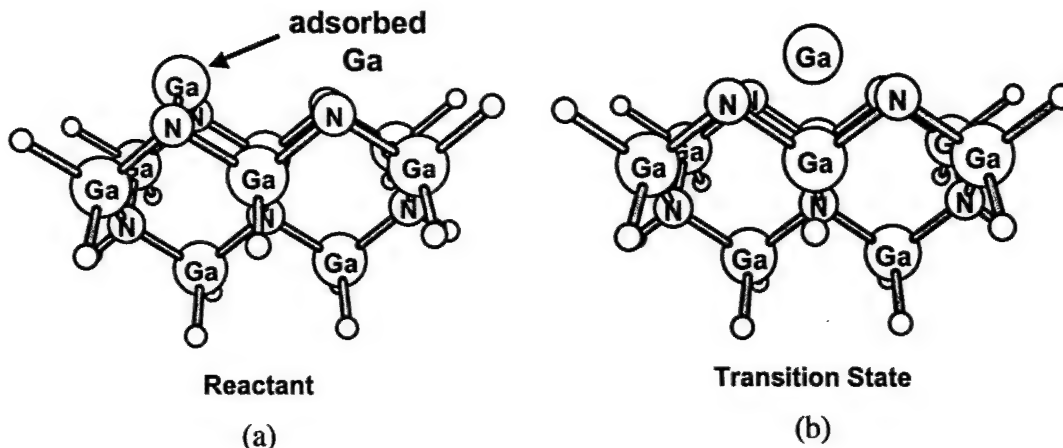
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Figure 7. Cluster model for surface diffusion: a) adsorbed Ga (reactant or initial state) and b) transition state for diffusion.

Figure 7b shows the transition state for Ga atom diffusion. At the transition state Ga atom is situated exactly at the middle point of the reactant and product. Figure 8 shows the effect of external field on the activation barrier. The activation barrier decreases continuously when field is pointing away from the GaN surface, while in other direction it increases initially and then decreases at very high field value. However, at all field range studied here, the former activation barrier remains always lower. This gives us an indication that the diffusion rate can be increased when field is pointing away from the surface. It should be pointed out that same direction of the external field results a decrease in bond energy also. So there is a distinct correlation between activation barrier and bond energy.
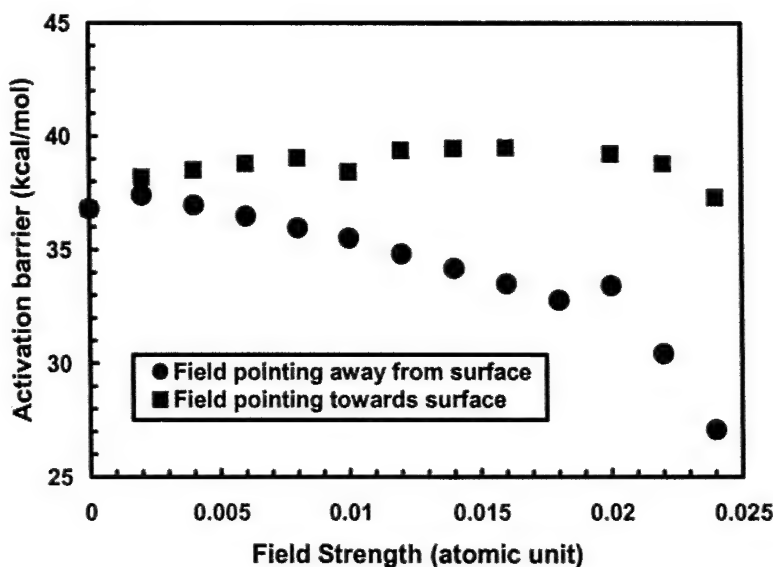

Figure 8. Variation of activation barrier with the strength of the external field in two different orientations. 1 atomic unit = 51.4 volt/angstrom

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4.1.4 Summary of Ab Initio Calculations Results

With ab initio quantum chemistry calculations, we have been able to establish a correlation between the bond strength with the orientation and the strength of the external field. We have then extended this idea to the activation barrier for surface diffusion. Our calculations showed that the activation barrier for surface diffusion decreases with an increase in the external field strength when field points away from the surface. This is analogous to the observation of our bond energy calculations. This establishes that fact that there is a distinct correlation between bond energy and activation barrier, and altering bond energy will alter the activation barrier. This calculation predicts the orientation of the external field that will decrease the activation barrier.

In the following sections, we present the KLMC method, and microstructures obtained using the ab initio calculated bond energies with and without application of external field.

4.2   Kinetic Lattice Monte Carlo Method

The computer code for KLMC method has been earlier developed by the group of Professor Dimitris Pavlidis, University of Michigan. [8]   Substantial modifications have been performed in order to incorporate the external field effect.

Simulation conditions

In this simulation, the growth of GaN is considered under MBE-like conditions. MOCVD is complex to simulate because of the various chemical reactions in it. ECR-MBE like conditions were used since molecular nitrogen does not chemisorb on GaN because of the strong bonding energy between two nitrogen atoms. In ECR-MBE, the ECR source provides atomic nitrogen. Gallium is provided by the conventional Knudsen effusion cell. In addition, GaN grows on the (001) GaAs substrate.

12 monolayers of 30×30 sites were simulated. Each monolayer has only one kind of atoms and the bottom layer is Nitride layer. Thus 2nd, 4th, 6th, 8th, 10th and 12th monolayers are filled with Ga atoms, and 1st, 3rd, 5th, 7th, 9th, and 11th layers are only composed of N atoms. In 2D and 3D contours in the simulation results show only even number monolayers containing gallium atoms. The unit of the gallium flux is monolayers per second. Therefore, if the Ga flux is 0.6, it is 30×30(atoms/monolayer) ×0.6(monolayers/second) = 540(atoms/second).

Conventional Monte Carlo Method

GaN growth can be explained by four basic events: impingement, incorporation, surface migration and evaporation. In conventional Monte Carlo analysis, the kinetic processes are considered as an individual event. A probability distribution function of each event happening is established considering the rates of each kinetic process, and then the probability distribution function is compared with the random number in order to decide which event will happen. In the GaN growth simulation, the conventional way is not appropriate to use because of the extremely high nitrogen evaporation and migration rate. If 10 monolayers of 30×30 site are simulated, more than 10^{12} events need to be simulated. Therefore a special Monte Carlo method is established for the GaN growth simulation.

Special Monte Carlo method

In the special Monte Carlo method, Gallium and Nitrogen incorporations are related by the following surface occupation probability function.

$$P_N(E_{tot})=J_N/R_e(E_{tot}) \tag{5}$$

where J_N is the nitrogen flux and $R_e(E_{tot})$ is the evaporation rate for the site with energy E_{tot}. Nitrogen is incorporated only when the random generated number is less than P_N. Consequently, incorporation and evaporation of N are not considered as an individual event and only the three events: incorporation Ga and N, migration of Ga, and evaporation of Ga are considered as an individual event in the simulation.

Gallium incorporation

As mentioned above, gallium incorporation is related with nitride incorporation. When Ga impinges to the substrate, it incorporates with two nitrides below. Because evaporation rate of nitride is very high, nitride can be incorporated only when trapped in the GaN structure as can be seen in the Figure 9. Figure 10 shows the flow chart of the Ga and N incorporation.
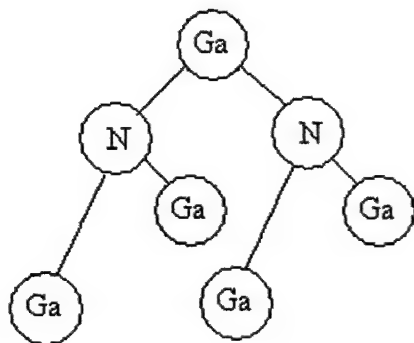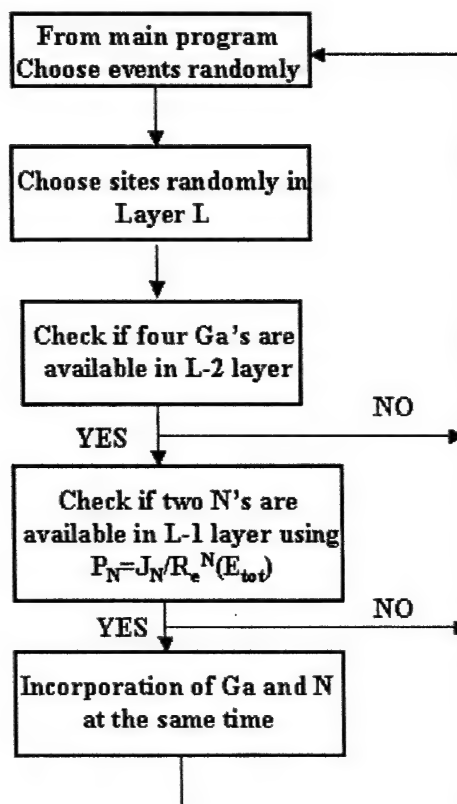

Figure 9. Nitrogen atoms trapped by gallium atoms

Figure 10. Flow chart for Ga & N incorporation.

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Gallium migration

Gallium migration rates are taken to be Arrhenius form as follows,

$$R_d{}^{Ga} = R_{od}{}^{Ga} exp(-(E_{tot}-\Delta)/k_B T) \qquad (6)$$

where $R_{od}{}^{Ga}$ is a prefactor, which is $3.5\times10^{10} s^{-1}$; $Etot$ is the total energy at the site of interest; Δ is an energy adjustment for a specific energy migration process and $(E_{tot}-\Delta)$ is the activation barrier for migrations. Gallium migration on the surface is composed of the four processes: (a) hopping on the same surface layer in a direction which is defined by the intercept of the surface and orbital planes; (b) hopping on the same layer in a direction which is perpendicular to the intercept line of the surface and orbital planes; (c) hopping to lower later (d) hopping to upper layer. Migration rate varies according to the process and $Etot$. For example, if the Ga has no second nearest bond on the same layer (adatom case),

$$E_{tot}=2V_{Ga-N} + 4V_{Ga-Ga}, \qquad (7)$$

and if Ga is at the kink site, it has two more second nearest bonds with Ga on the same layer and

$$E_{tot}=2V_{Ga-N} + 6V_{Ga-Ga}. \qquad (8)$$

Even though gallium atom moves to the other site, it always maintains one or more bonds with the atoms previously connected, in the migration equation, Δ is the maintained bonding energy.

Figure 11 and Figure 12 show the migration process (a) and (b) respectively. The energy barrier for the migration process (a) is equal to breaking one Ga-N bond and two Ga-Ga bonds. In the case of process (b), two Ga-N bonds and two Ga-Ga bonds breaking is needed. Therefore, the rate of process (a) is much larger than process (b). As can be seen in Figure 13, lower layer hopping to the eight sites is possible. The black spots are possible sites for lower layer hopping. In this case, only one Ga-Ga bond is maintained. Hence the more energy barrier than the same layer hopping the lower layer hopping has. Upper layer hopping has similar process with lower layer and has also high energy barrier. Figure . 14 summarizes the migration processes.
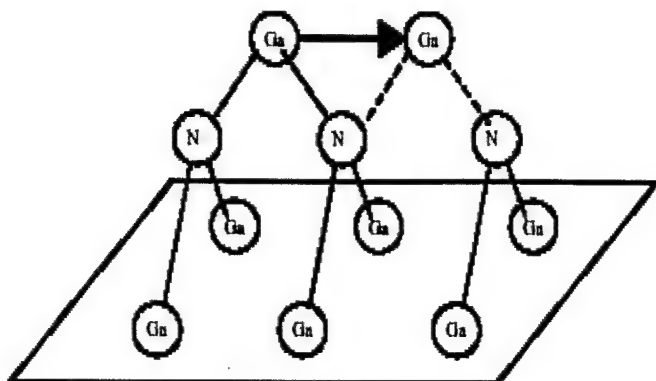
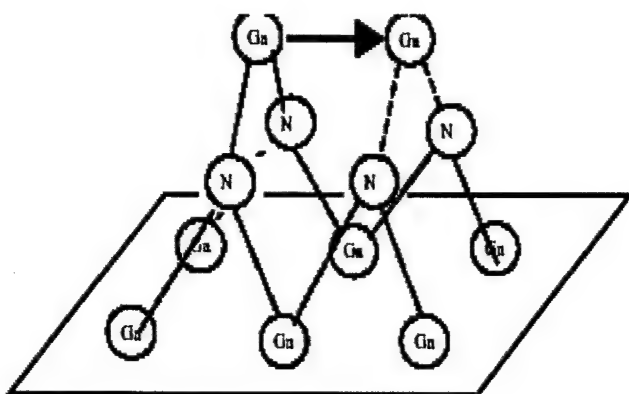Figure 11. Same layer migration breaking one Ga-N bond

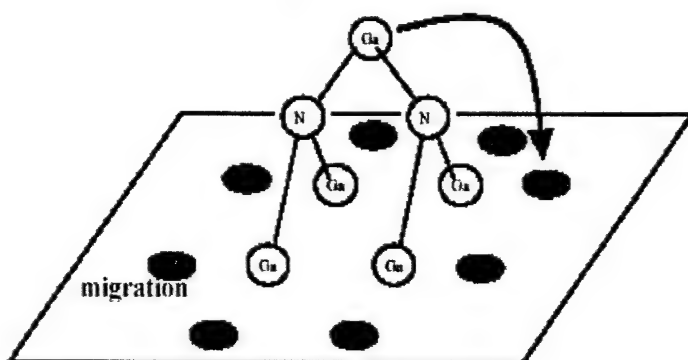Figure 12. Same layer migration breaking two Ga-N bond
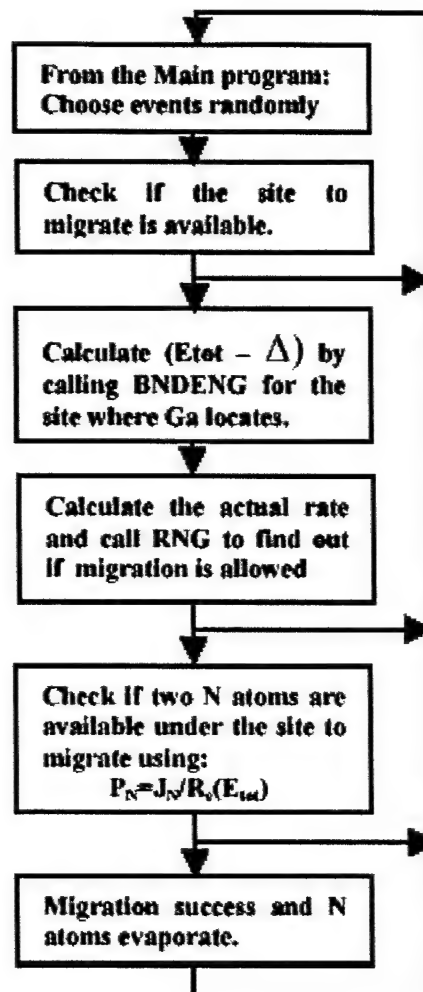
Figure 13. Lower layer migration

From the Main program: Choose events randomly

Check if the site to migrate is available.

Calculate (Etot − Δ) by calling BNDENG for the site where Ga locates.

Calculate the actual rate and call RNG to find out if migration is allowed

Check if two N atoms are available under the site to migrate using:
$P_N = J_N / R_s(E_{tot})$

Migration success and N atoms evaporate.

Figure 14. Flow chart for migration

<u>Gallium and nitrogen evaporation</u>
The evaporation rates of Ga and N atoms, similar to the migration rate, are

$$R_e^{Ga} = R_{oe}^{Ga}\exp(-E_{tot}/k_BT) \ \& \ R_e^{N} = R_{oe}^{N}\exp(-E_{tot}/k_BT) \tag{8}$$

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where R_{oe}^{Ga} and R_{oe}^{N} are prefactors for each equation whose values are 8×10^{13} S^{-1} and 1.35×10^{22} S^{-1} respectively.

Because of the very high evaporation rate of nitride, gallium evaporation and nitride evaporation are related also. If Ga atom evaporates, two nitrides under the Ga atom also evaporate at the same time. Figure 15 shows the conceptual diagram of evaporation and Figure 16 is a flow chart of evaporation.
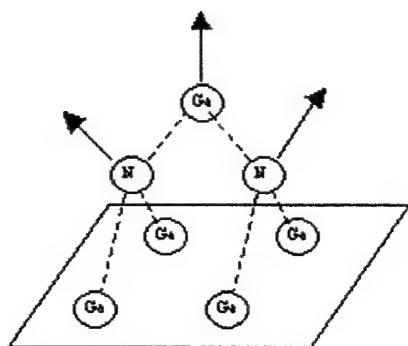

Figure 15. Ga and N evaporation
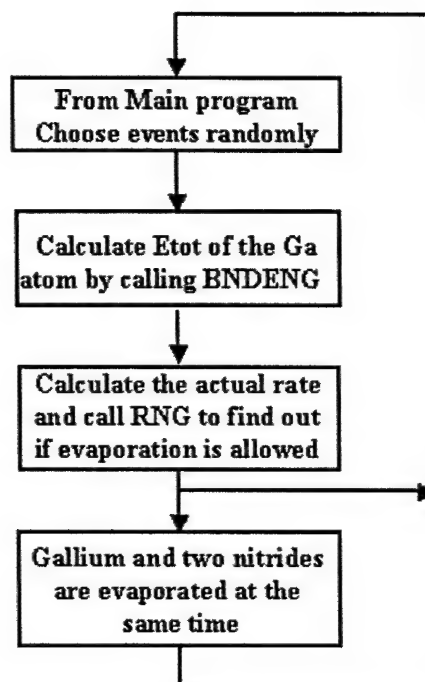
Figure 16. Flow chart for Ga and N evaporation

4.2.1   Simulation Results Without External Field

The above methodology has been implemented in a KLMC code. The following sections, we describes the results of surface morphology calculations using KLMC method without and with the application of external field.

Impact of N/Ga flux ratio on the growth rate

First of all, the relation between V/III ratio and growth rate was investigated when the substrate temperature varied. At a fixed temperature, as V/III increases, growth rate increases linearly and reaches to saturation value, which is determined by the Ga flux (Figure 17). Thus, maximum growth rate always be less than Ga flux. The V/III ratio at which saturation value is reached is determined by the substrate temperature
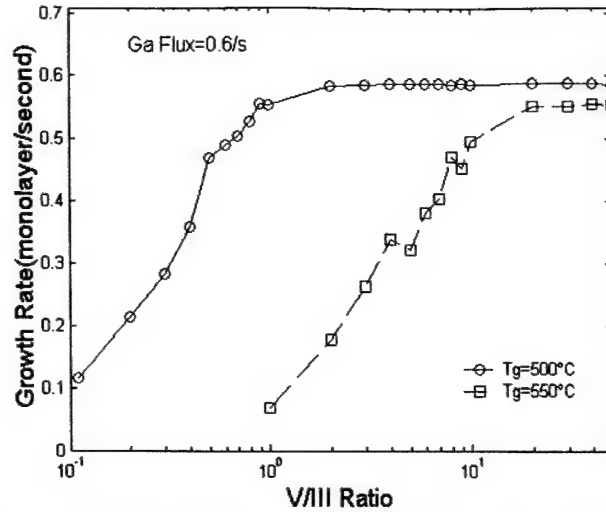
Figure 17. Growth rate vs. V/III ratio (Ga flux=0.6/s)

Impact of the substrate temperature on the growth front

Figure 18 shows [nth layer coverage(dq_n)]/[total coverage(dq_{tot}) as a function of growth time for constant Ga flux and V/III ratio.(dq_n/dq_{tot}) means the ratio of the additional incorporated atoms in the nth layer with respect to the total incorporated atoms within a time interval dt. In order to get a smooth growth surface, layer-by-layer growth should occur and no overlap between the successive graphs. Figure 19 shows three dimensional and two dimensional contour plots of the surface. ML indicates a growth front monolayer. The higher ML, the rougher the growth front is.
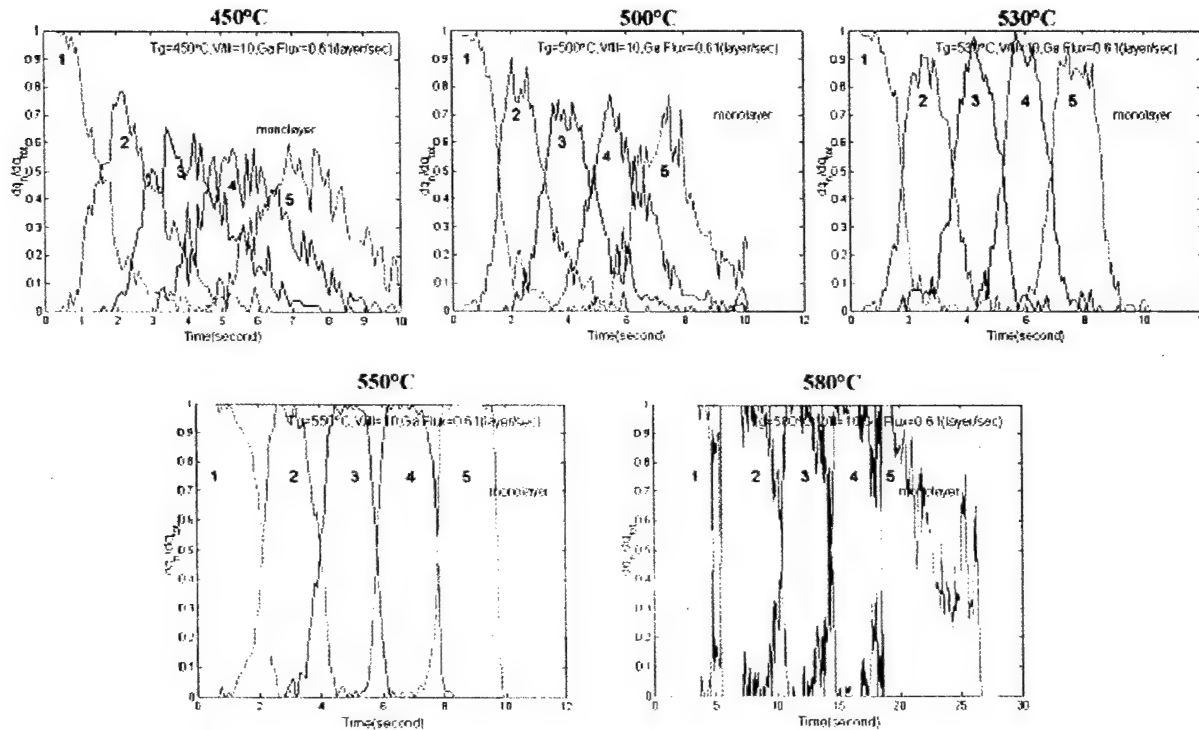

Figure 18. Ratio of nth layer coverage over total coverage vs. growth temperature
(Ga flux=0.61/s, V/III=10)

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As temperature increases, the growth front gets better. At given Ga flux and V/III ratio, we can get the best front at 550°C. A temperature goes over 550°C, growth rate drastically decreases and at some point Ga atoms cannot incorporate because the evaporation rate of nitride atom gets too high. This means that nitride atoms evaporate so fast that gallium atoms cannot trap them.
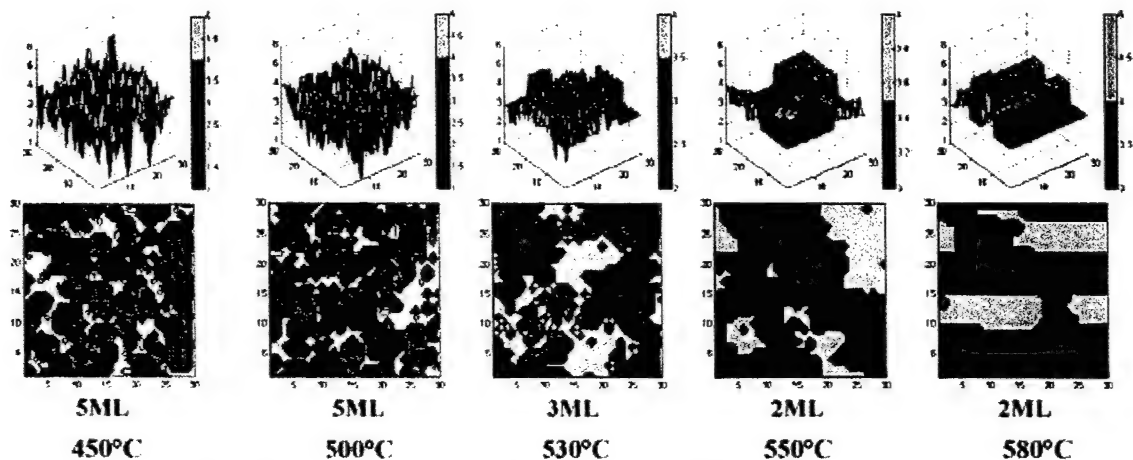

| 5ML | 5ML | 3ML | 2ML | 2ML |
| 450°C | 500°C | 530°C | 550°C | 580°C |

Figure 19. 3D and 2D contours of the surface vs. temperature increases
(Ga flux=0.61/s, V/III = 10)

Impact of V/III flux ratio on the growth front

In order to study the impact of the V/III ratio on the growth front and the growth ratio, the Ga flux was fixed at 0.6/s and the temperature was kept constant at 650°C. When the V/III ratio increases, the growth front gets rougher (Figures 20 and 21). Thus a smaller V/III ratio is suitable for a smooth growth front, but when the V/III ratio is too low, the growth rates becomes too low.
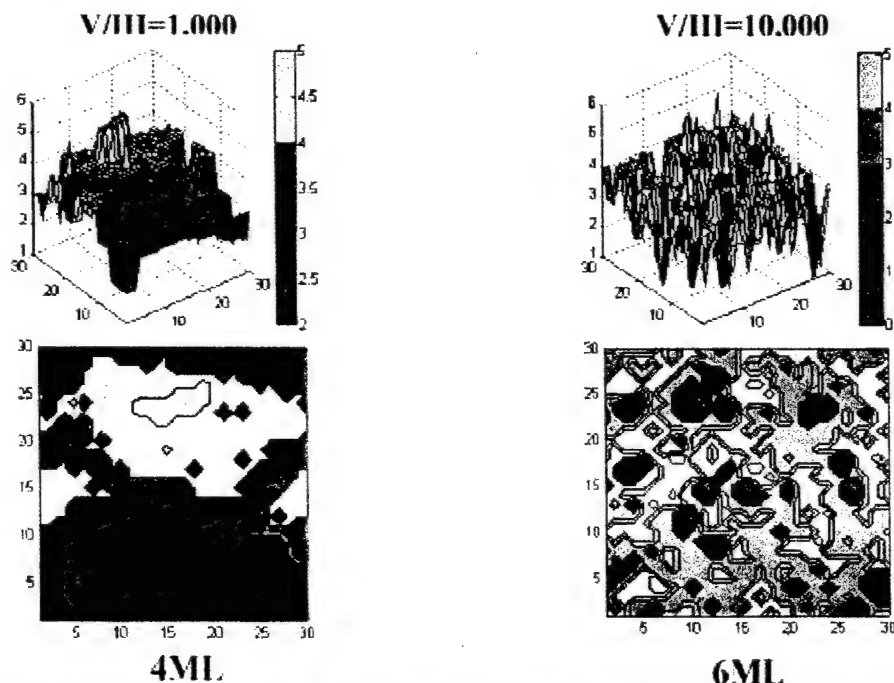

V/III=1.000   **V/III=10.000**

4ML   **6ML**

Figure 20. 3D and 2D contours of the surface vs. V/III ratio (Ga flux=0.61/s, T=650°C)
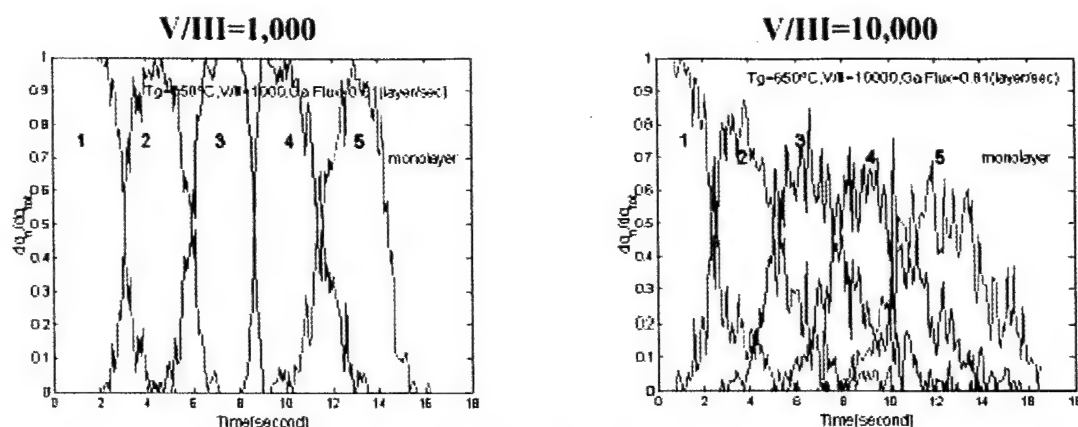
17

V/III=1,000

V/III=10,000

Figure 21. Ratio of nth layer coverage over total coverage vs. growth temperature
(Ga flux=0.61/s, T=650°C)

Impact of Ga and N flux on the growth rate and the roughness of the growth front

As stated earlier, the growth rate is dependant on the Ga flux. As the Ga flux increases, the growth rate increases; however, the growth front gets rougher. This can be proven by Figures 22 and 23. As can be seen at Figure 23, at a given temperature 650°C, Growth rate get saturated to the value of Ga flux or less. Figure 23 shows us that the higher Ga flux, the rougher the growth front.
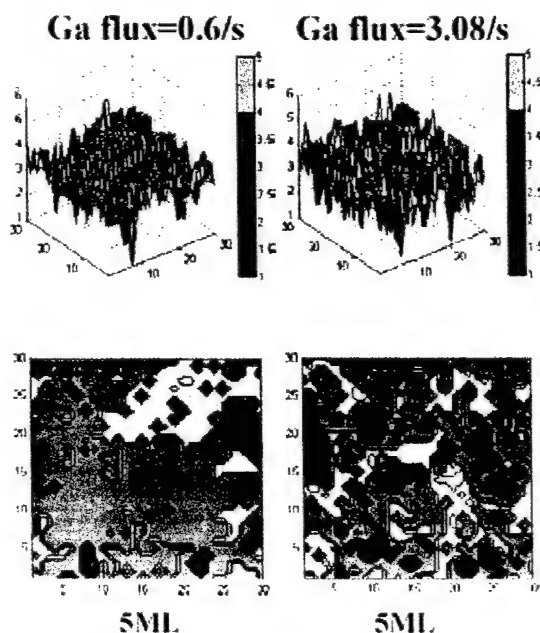
Ga flux=0.6/s   Ga flux=3.08/s

5ML   5ML

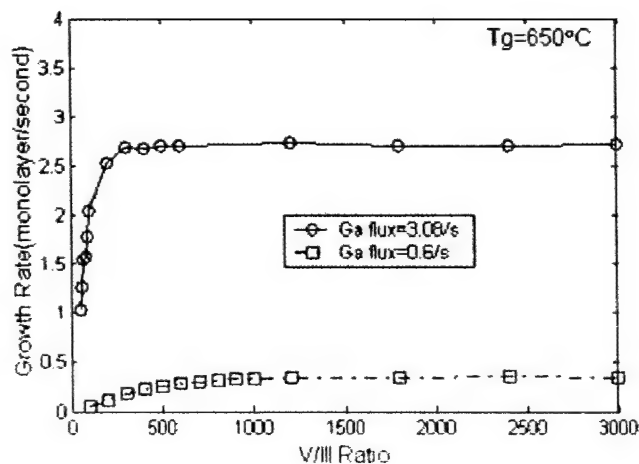*Figure 22. Growth front contour and 3D plot*
(T=650°C, V/III=10)

Figure 23. Growth ratio vs. Ga flux and V/III ratio

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4.2.2 Simulation Results With Electric Field

The applied electric field on the growth front primarily affects the bonding energy between gallium and nitride atoms. When a positive electric field is applied, the bond energy is reduced while when a negative direction electric field is applied, it increases the bonding energy. Field dependent bonding energy values were applied to the simulation. Also, the roughness of the growth surface was calculated in order to see the improvement of growth front quality. The roughness can be expressed as:

$$\text{Roughness} = [\ \Sigma (n(i,j)-na)2\ /ntot]^{1/2} \tag{9}$$

where $n(i,j)$ is the height of cation layers at $site(i,j)$, na is the average height of Ga layers, and $ntot$ is the total number of gallium atoms in one layer.
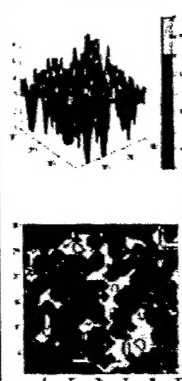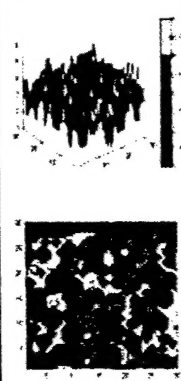
E-field	0 a.u	0.002a.u	0.004a.u	0.006a.u	0.008a.u
Growth Front					Growth is too slow
Roughness	1.546	1.457	0.998	0.298	

Figure 24. Application of electric field in (+) direction (pointing away from the surface)
(1a.u = 51.4 V/angstrom)

Simulations were performed at 400°C with Ga flux of 0.6layers/second and V/III ratio of 10. Inputs for the simulations (such as bond energy) at different field strength were obtained from the ab initio calculation (Figure 4). As the electric field increases, the roughness decreases and the growth front improves (Figure 24). However, the growth rate becomes smaller as the electric field increases, and when over 0.008a.u of electric field is applied, growth cannot be seen. Therefore, it can be seen there is a direct relation between the bond energy and the surface morphology of the film. In the above case, the bond energy actually decreases with increases in field strength. This leads to lowering of activation barrier for diffusion, and consequently results in a smoother film.
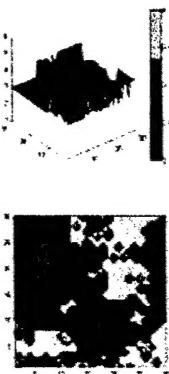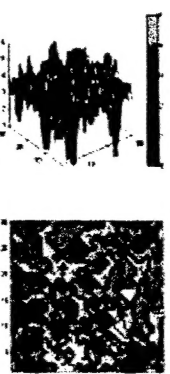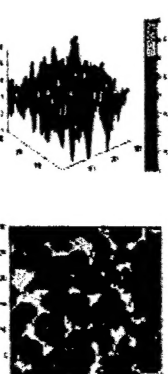
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E-field	0 a.u	-0.002a.u	-0.004a.u	-0.006a.u	-0.008a.u
Growth Front	Growth is too slow				
Roughness		0.611	1.119	1.558	1.523

Figure 25. Application of Electric field in (-) direction (pointing towards the surface)
(1a.u = 51.4 V/angstrom)

We then performed simulation when the field is pointing towards the surface. One may recall from the ab initio calculations that the bond energy increases with increase in field strength at this orientation. This means that the surface diffusion rate becomes smaller with increases in field strength. In the simulations, the temperature was kept at 600°C, Ga flux was fixed 0.61layers/second, and V/III ratio was 10. One can see from Figure 25 that as the electric field increases in magnitude, the growth front becomes rougher, but the growth rate increases. These results clearly indicate there is a direct correlation between the direction and strength of the external field and surface morphology. Therefore, one can obtain desired the surface morphology by applying the external field in a controlled manner.

Summary of KLMC Simulations
A special Monte Carlo method was developed and used to investigate the impacts of the substrate temperature, Ga flux, and V/III ratio on the GaN growth front and the growth rate, both in absence and presence of external field. In absence of external field, when Ga flux and V/III ratio are fixed, the higher temperature, the better growth front; however over certain temperature, growth rate is too low to real applications because of the high nitride evaporation rate. At a given temperature and V/III ratio, the lower Ga flux, the better growth front, but the lower the growth rate. Also at a fixed temperature and Ga flux, the lower V/III ratio, the growth front gets better but growth rate get lower.

First studies of the impact of external energy by the presence of electric field were performed to investigate the possibility of controlling the growth front quality. The growth rate becomes smaller as the magnitude of a positive electric field increases, and growth can cease at high electric fields. In case of a negative electric field, as the electric field increases in magnitude, the growth front becomes rougher, but the growth rate increases.

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5. CONCLUSIONS/ACHIEVEMENT

First principle ab initio quantum chemical methods has been applied to investigate the influence of the external field and its orientation on the bond energy of GaN and activation barrier for surface diffusion. Our calculations showed that one can really reduce or increase the bond energy and activation barrier by applying external field. The direction of the external field is very important in determining its effect on bond energy and activation barrier. At the end of the Phase I project, we are able to establish a correlation between the bond energy/activation barrier and the strength and orientation of the external field. The results of ab initio calculations were then fed in the KLMC calculations to simulate the surface morphology. KLMC calculations predict that the roughness of a film can be controlled by controlling the strength and orientation of the external field. Overall, we have been able to establish a correlation between the strength and orientation of an external field with surface roughness of a thin-film.

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